

947

AIR QUALITY SURVEY (TAGA 6000)
SERVAAS RUBBER CANADA INC.,
CORNWALL
AUGUST - SEPTEMBER, 1989

FEBRUARY 1990



Ontario

Environment
Environnement

Jim Bradley, Minister/ministre

SURVEY REPORT

AIR QUALITY SURVEY (TAGA 6000)

SERVAAS RUBBER CANADA INC., CORNWALL

AUGUST - SEPTEMBER, 1989

ARB-032-90

Report prepared for:
Southeastern Region

Report prepared by:
Gary B. De Brou
and
Andy C. W. Ng
Air Resources Branch

FEBRUARY 1990



Copyright: Queen's Printer for Ontario, 1990
This publication may be reproduced for non-commercial purposes
with appropriate attribution.

Executive Summary

During the period of August 29 to September 8, 1989, the mobile TAGA 6000 unit of the Air Resources Branch performed an air quality survey in Cornwall, at the request of the Southeastern Region. The survey objective was to identify and determine the ambient concentrations of the odorous pollutants in the vicinity of the SerVaas Rubber Canada plant located at 600 Campbell Street.

An unpleasant odour was frequently present downwind of the SerVaas plant during the monitoring periods of August 30, 31, and September 6 and 7. Fingerprint mass scan data highlighted two major groups of contaminants: benzothiazoles and amines. Dimethylformamide, dimethylacetamide and aniline were also detected downwind of SerVaas Rubber Canada, Inc.

A total of 27 half-hour average concentrations of benzothiazole and methylbenzothiazole were determined. The ambient benzothiazole concentrations ranged from "not detected" to $5 \mu\text{g}/\text{m}^3$. The provisional guideline for benzothiazole, $200 \mu\text{g}/\text{m}^3$, is based on health effects.

Amines, mainly dimethylamine and trimethylamine, were also detected in low concentrations downwind of the SerVaas plant throughout the monitoring period. Twenty-seven half-hour average concentrations of trimethylamine were determined during the survey. The trimethylamine levels ranged from 0.5 to $1.8 \mu\text{g}/\text{m}^3$ for a half-hour average. The Ministry guideline for trimethylamine, $0.5 \mu\text{g}/\text{m}^3$, is based on odour.

Table of Contents

| | |
|---|----|
| 1.0 Introduction | 1 |
| 2.0 The TAGA 6000 "Fingerprinting" Technique | 1 |
| 2.1 Quantitation of Target Compounds | 2 |
| 2.2 Survey Strategy | 3 |
| 3.0 Results and Discussion | 3 |
| August 30 | 4 |
| August 31 | 4 |
| September 6 | 4 |
| September 7 | 4 |
| 4.0 Summary and Conclusions | 5 |
| 5.0 Acknowledgements | 6 |
| 6.0 Appendices | 13 |
| 6.1 Appendix A: Plant Process and Relevant Production Information | 13 |
| 6.2 Appendix B: TAGA 6000 Library Search Daughter Ion Scans of the Odour Fingerprint Compounds, SerVaas Rubber, Cornwall | 15 |

List of Tables

| | |
|--|----|
| Table 1: TAGA 6000 Odour Fingerprints, SerVaas Rubber, Cornwall | 7 |
| Table 2: Half-hour Average Concentrations of Benzothiazole | 8 |
| Table 3: Half-hour Average Concentrations of Methylbenzothiazole | 9 |
| Table 4: Half-hour Average Concentrations of Trimethylamine | 10 |

List of Figures

| | |
|--|----|
| Figure 1: Schematic of the TAGA 6000 System | 11 |
| Figure 2: Map of the Monitoring Sites at SerVaas Rubber Canada Plant | 12 |

1.0 Introduction

At the request of the Southeastern Region, the mobile TAGA 6000 unit of the Air Resources Branch recently conducted an air monitoring survey in Cornwall in the vicinity of SerVaas Rubber Canada, Inc. The SerVaas plant is located at 600 Campbell Street. The plant recycles butyl inner tubes by a thermal devulcanisation process. The end product is isoprene rubber. A brief description of the plant process and the relevant production information is supplied in Appendix A.

Presented below is the analysis of air samples acquired downwind of the SerVaas plant as determined in the field by the mobile TAGA 6000 unit during the survey period of August 29 to September 8, 1989.

2.0 The TAGA 6000 "Fingerprinting" Technique

The Trace Atmospheric Gas Analyzer (TAGA) is a specialized tandem mass spectrometer (MS/MS) with a unique air sampling inlet system and ion source (see Figure 1). Ambient air is sampled directly at a high flow rate (100 l/min.) into the ion source, which is operated at atmospheric pressure. Ionisation of trace contaminants is achieved by chemical ionisation (CI) initiated by a corona discharge. Selective ionisation of chemical classes is achieved through the addition of an appropriate CI reagent to the flowing air sample. For example: atmospheric water vapour highlights ketones, aldehydes, alcohols and acids; oxygen highlights phenols, chlorophenols and acids; benzene highlights aromatic compounds and sulphurous species; and ammonia highlights amines, amides and some ethers.

The ionisation of pollutants yields a mixture of pseudo-molecular ions which are immediately subjected to mass analysis up to 250 atomic mass units (amu). Mass "fingerprinting" is achieved in a matter of minutes. The chemical or pollutant fingerprint is derived from the interpretation of all the mass spectra for a given monitoring period. Identifications based on this method are tentative, as they are determined through considerable interpretation by the scientist. The identity of compounds present at concentrations greater than about $1 \mu\text{g}/\text{m}^3$ can be confirmed by use of the second stage of mass analysis to obtain a "daughter ion" mass spectrum. In this technique, the preselected ions collide with an inert gas in the mass spectrometer and subsequently undergo collisionally activated dissociation (CAD). The pattern of fragmentation is characteristic of the compound which produced the pseudo-molecular ion. The daughter ion spectra produced in the field may be computer searched against a library of known daughter ion spectra in near real-time, allowing on-site confirmation of pollutant identification (Examples of CAD spectra are provided in Appendix B). In addition, the ambient air may be screened for classes of pollutants using either a "neutral loss" scan or a "parent ion" scan. For example, it is possible to screen for chlorinated species by monitoring the neutral loss of 35 amu, the mass of the more abundant isotope of chlorine.

The presence of methyl ketones could be established by performing a parent ion scan for 43 amu, the atomic mass of a daughter ion common to all methyl ketones.

Owing to this system's unique features of direct air sampling and atmospheric pressure chemical ionisation, the technique is highly sensitive to many polar organic compounds in real-time. Generally, the TAGA can detect volatile compounds which contain a heteroatom such as N, O, P, S, or a halide. The real-time limits of detection for the TAGA range from 0.1 to 10 $\mu\text{g}/\text{m}^3$, depending on the type of chemical and the complexity of the sample matrix.

The mobile TAGA 6000 unit is equipped with a meteorological station which monitors atmospheric temperature at the roof height and the wind speed and direction at ten metres. Meteorological data can be simultaneously recorded by the TAGA system computer along with air quality measurements.

2.1 Quantitation of Target Compounds

Accurate quantitation of a target compound can be achieved by calibrating the response of the TAGA to known gas phase concentrations of the target compound. Fragment ions, produced through collisions with argon molecules in quadrupole 2 (see Figure 1) are characteristic of the target compound monitored in the "multiple reaction monitoring" (MRM) mode. A typical monitoring period for obtaining quantitative data is thirty minutes; this conforms to the period specified for Ministry standards and guidelines for atmospheric pollutants. The instrument is calibrated at least twice a day, usually before and after the monitoring period. Calibrations are conducted more frequently in instances where target compound concentrations exceed Ministry standards and guidelines.

Prior to any downwind monitoring of the SerVaas plant, a four point calibration was performed to determine the sensitivity of the TAGA 6000 towards gaseous benzothiazole and methylbenzothiazole. Two sets of parent-daughter ion pairs ($M1/M3 = 136/45$, $136/65$, $136/77$, and $136/109$, and $M1/M3 = 150/65$ and $150/109$, see Appendix B) were chosen to verify the concentrations of benzothiazole and methylbenzothiazole respectively in the air samples. The sensitivities of the TAGA 6000 toward benzothiazole and methylbenzothiazole were determined by the slopes of the calibration curves. Calibrations were performed three times to assess reproducibility. Similarly, another set of calibrations were performed at the end of each monitoring day to ensure that the benzothiazole response factors were within QA/QC criteria. On days when monitoring was restricted to one or two half-hour periods, the second calibration was not required.

Two parent-daughter ion pairs ($M1/M3 = 60/45$ and $60/44$, see Appendix B) were used to determine the half-hour average concentrations of trimethylamine. Trimethylamine could not be calibrated during the survey period in Cornwall. Therefore, the data reported for trimethylamine were based on the calibrations performed after the

survey.

2.2 Survey Strategy

The basic survey strategy was to position the TAGA 6000 downwind of SerVaas and obtain chemical fingerprints of the odours, and subsequently quantify the ambient concentrations of the most abundant pollutants. In addition to the downwind (source) monitoring, air monitoring was performed at locations upwind of the suspected source. The upwind data was used to: determine background contributions to fingerprint mass scans, determine the detection limit of the target compound, and to correct quantitative downwind measurements for background contributions. The selection of monitoring sites was based upon several observations: wind direction and wind speed, odour characteristics, type of chemicals detected (fingerprint), plume tracking information, and accessibility and road network.

3.0 Results and Discussion

The mobile TAGA 6000 unit conducted ambient air monitoring in Cornwall during the period of August 29 to September 8, 1989. During the monitoring period, the prevalent winds were from the west. Thus the monitoring sites were limited to Loyalist Street, south and east of the plant (see Figure 2). Plume tracking was not performed due to the insufficient road network downwind.

An unpleasant odour was frequently present downwind of the plant. A total of 8 fingerprints of the ambient air were determined at locations downwind of the plant (see Table 1). All major peaks from the APCI/MS of the background subtracted mass spectra was subject to MS/MS analysis. The daughter ion spectrum was computer searched against a library of known daughter ion spectra to identify the compound (see Appendix B). Table 1 also provides estimates of the ambient levels of the fingerprint chemicals. Each estimated concentration is based on the average of five instantaneous measurements taken within a 25 second interval.

On August 30, 31, and September 6 and 7, a total of 27 half-hour average concentrations for ambient benzothiazole and methylbenzothiazole were measured at 4 locations downwind of the plant (see Figure 2). The benzothiazole and methylbenzothiazole half-hour average concentrations are summarized at Table 2 and Table 3, respectively. Also included in these tables are information regarding sampling periods, sampling locations, meteorological conditions, and daily detection limits for the benzothiazoles. All data is corrected for background or upwind contributions.

Trimethylamine, with a low Ministry guideline of $0.5 \mu\text{g}/\text{m}^3$, was measured simultaneously with the benzothiazoles. Twenty-seven half-hour average concentrations of trimethylamine were reported. Trimethylamine could not be calibrated during the

survey period in Cornwall. Therefore, the data reported for trimethylamine were based on calibrations performed after the survey. The half-hour average concentrations are summarized in Table 4.

August 30

This day the sky was partially cloudy with winds out of the west at 5 to 30 km/h. Upwind measurements and background fingerprints were recorded at St. Peter's Church parking lot, corner of Second Street and Campbell Street. The TAGA unit was then moved to the open space east of SerVaas plant entrance off Loyalist Street (Site 4) downwind of the plant. An unpleasant odour was present at this location. Three sets of chemical fingerprints (F01 to F03) were acquired. At 12:30, the winds shifted to the NW, thus, the TAGA unit moved to the south side on Loyalist Street, opposite the entrance (Site 1). Two additional chemical fingerprints (F04, F05) were determined. Also two half-hour average concentrations of target compounds (S01, S02), benzothiazole, methylbenzothiazole and trimethylamine, were collected in the presence of the SerVaas odour.

August 31

August 31 was a sunny day with W to NW winds at 10 to 20 km/h. At 8:50 the TAGA unit was stationed on Loyalist Street (Site 1). The SerVaas plant was at the end of an autoclave cycle. Two sets of chemical fingerprints (F06, F07) and one half-hour average concentrations of the target compounds (S03) were acquired in the presence of the odours. The TAGA unit then moved to the NW corner of the same industry complex next to Campbell Street for background measurements and both benzothiazole calibrations. A chemical fingerprint (F08) and five half-hour average concentrations of target compounds (S04 to S08) were collected at the south side on Loyalist Street (Site 2), approximately 20m west of Site 1. During the sampling period odours were observed to be unpleasant yet not particularly strong.

September 6

This was an overcast day with winds from the S to SW at 0 to 15 km/h. Background measurements and benzothiazole calibrations were made at the parking lot of St. Peter's Church, upwind of SerVaas. The TAGA unit then moved to a downwind location, end of Simmons Pl., roughly 30m NE of SerVaas (Site 3). A total of 8 half-hour average concentrations of target compounds (S09 to S16) were taken in the presence of a slight odour.

September 7

September 7 was a sunny day with winds from the W to SW at 2 to 15 km/h.

Background measurements and benzothiazole calibrations were made at the St. Peter's Church parking lot, upwind of SerVaas. Five half-hour average concentrations of the target compounds (S17 to S21) were collected on Loyalist Street, 100m east of SerVaas (Site 1). This was the only location downwind of SerVaas where odour was discernible. The TAGA unit then moved to the north side on Loyalist Street, 5m east of the SerVaas driveway entrance (Site 4). Six more half-hour average concentrations of the target compounds (S22 to S27) were acquired in the presence of slight, unpleasant odour.

4.0 Summary and Conclusions

The mobile TAGA unit conducted an air monitoring survey in Cornwall, Ontario on August 29 to September 8, 1989 at the request of the Ministry's Southeastern Region. The primary purpose of this survey was to identify and to determine the ambient concentrations of the contaminants downwind of SerVaas Rubber Canada plant. The monitoring results indicated that benzothiazoles and amines were the major groups of contaminants detected by the TAGA downwind of the SerVaas Rubber Canada plant.

Dimethylamine, trimethylamine, dimethylformamide, dimethylacetamide, benzothiazole, methylbenzothiazole and aniline were detected downwind of SerVaas Rubber in the presence of unpleasant odour. Eight sets of chemical fingerprints were acquired on August 30 and 31. The estimated concentrations, based on the averages of 5 instantaneous measurements taken over a period of 25 seconds, ranged between 12 to 68 $\mu\text{g}/\text{m}^3$ for dimethylamine, 3 to 26 $\mu\text{g}/\text{m}^3$ for trimethylamine, 9 to 26 $\mu\text{g}/\text{m}^3$ for dimethylformamide, 1 to 8 $\mu\text{g}/\text{m}^3$ for dimethylacetamide, 2 to 11 $\mu\text{g}/\text{m}^3$ for benzothiazole, 1 to 3 $\mu\text{g}/\text{m}^3$ for methylbenzothiazole, and 1 to 4 $\mu\text{g}/\text{m}^3$ for aniline.

Twenty-seven (27) half-hour average concentrations for trimethylamine, benzothiazole and methylbenzothiazole were also recorded downwind of the SerVaas plant on August 30, 31, and September 6 and 7. The half-hour average concentrations for benzothiazole ranged from not detected to 5 $\mu\text{g}/\text{m}^3$. Of the total 27 half-hour average concentrations for benzothiazole, two were measured at 5 $\mu\text{g}/\text{m}^3$, five were detected but below the quantitation limit and the remaining, twenty, were below the detection limits. The maximum instantaneous concentration for benzothiazole, 20 $\mu\text{g}/\text{m}^3$ was measured on August 31. The provisional guideline for benzothiazole, 200 $\mu\text{g}/\text{m}^3$, is based on health effects.

All of the 27 half-hour average concentrations for methylbenzothiazole were below the quantitation limits, typically 1 $\mu\text{g}/\text{m}^3$. The maximum instantaneous concentration for methylbenzothiazole, 6 $\mu\text{g}/\text{m}^3$, was measured on September 6.

The half-hour average concentration of trimethylamine, based on the calibrations performed after the survey, ranged from 0.5 $\mu\text{g}/\text{m}^3$ to 1.8 $\mu\text{g}/\text{m}^3$ acquired downwind of the SerVaas Rubber Canada plant. The maximum instantaneous concentration of

trimethylamine, $11 \mu\text{g}/\text{m}^3$, was measured on September 6. The Ministry guideline for trimethylamine, $0.5 \mu\text{g}/\text{m}^3$, is based on odour. Trimethylamine was the only contaminant recorded downwind of SerVaas at limits exceeding the Ministry guidelines and odour threshold values published in scientific literature.

5.0 Acknowledgements

The authors wish to thank the following contributors to this survey:

Roger Mercer (Consultant)
Jennifer Townsend (Consultant)
Robert Tooley (Consultant)
Mike Ladouceur (MOE)
Rheal Delaquis (MOE)

Table 1: TAGA 6000 Odour Fingerprints, SerVaas Rubber, Cornwall.

| Date (1989) | Fingerprint number | Monitoring Period | Location ¹ | Dimethyl amine | Trimethyl amine | Detected Compounds ² , Estimated Concentrations ($\mu\text{g}/\text{m}^3$) | n,n-Dimethyl formamide | Dimethyl acetamide | 2-Benzothiazole | 2-Methyl benzothiazole | Aniline | Comments |
|--------------------------------|-----------------------|----------------------|-----------------------|-------------------|--------------------|---|---------------------------|-----------------------|-----------------|---------------------------|-------------------|----------------|
| Aug. 30 | F01 | 09:32 | 4 | 12 | 7 | 20 | 3 | 3 | 7 | 3 | 2 | moderate odour |
| Aug. 30 | F02 | 09:55 | 4 | 14 | 6 | 10 | 2 | 2 | 5 | 2 | 1 | moderate odour |
| Aug. 30 | F03 | 12:03 | 4 | 66 | 10 | 16 | 2 | 2 | 4 | 1 | 1 | moderate odour |
| Aug. 30 | F04 | 12:32 | 1 | 49 | 5 | 12 | 2 | 2 | 2 | 1 | 1 | moderate odour |
| Aug. 30 | F05 | 14:12 | 1 | 68 | 7 | 14 | 2 | 2 | 5 | 2 | 1 | moderate odour |
| Aug. 31 | F06 | 08:52 | 1 | 17 | 6 | 16 | 2 | 2 | 5 | 2 | 1 | moderate odour |
| Aug. 31 | F07 | 10:00 | 1 | 76 | 26 | 46 | 8 | 8 | 11 | 3 | 4 | strong odour |
| Aug. 31 | F08 | 12:36 | 2 | 34 | 3 | 9 | 1 | 1 | 4 | 2 | 1 | moderate odour |
| Ministry Criteria ⁴ | | | | | | | | | | | | |
| Odour Threshold ⁵ | | | | NA | 0.5(G) | 900(TS) | NA | 200(PG) | NA | NA | NA | |
| | | | | 650 ^a | 0.5 ^b | 30000 ^b | 170000 ^b | | NA | NA | 1200 ^a | |

1. See Figure 2 for monitoring locations.

2. Identifications confirmed by APCI/MS/MS.

3. Based on the average of 5 readings taken over a period of 25 seconds.

4. In $\mu\text{g}/\text{m}^3$, (G) = EASSC guideline, (TS) = EASSC tentative design standard, (PG) = EASSC provisional guideline.5. In $\mu\text{g}/\text{m}^3$, population perception threshold. *Compilation of Odour Threshold Values in Air and Water*, L.J. van Gemert, ed., National Institute for Water Supply, Voorburg, Netherlands, 1977. (a) = detection and (b) = recognition odour threshold values.

Table 2: Half-hour Average Concentrations of Benzothiazole.

| Date (1989) | Sample Number | Monitoring Period | Location ¹ | Meteorological AT | WS | Conditions ² WD | 2-BZT ³ ½hr Conc. | Det. ⁴ Limit | Max ⁵ Conc. | Error ⁶ (RSD%) | Comments |
|----------------|------------------|----------------------|-----------------------|----------------------|-------|-------------------------------|---------------------------------|----------------------------|---------------------------|------------------------------|-----------------------------|
| Aug. 30 | S01 | 12:41-13:11 | 1 | 26 | 20-40 | W-NW | DET ⁷ | NA ⁸ | 12 | NA | moderate odour ⁹ |
| Aug. 30 | S02 | 13:12-13:42 | 1 | 25 | 20-30 | W-NW | DET | NA | 13 | NA | moderate odour ⁹ |
| Aug. 31 | S03 | 09:27-09:57 | 1 | 20 | 10-20 | W-NW | 5 | 1 | 20 | 4 | moderate odour |
| Aug. 31 | S04 | 12:50-13:20 | 2 | 24 | 10-25 | W-NW | ND ¹⁰ | 1 | 9 | 4 | moderate odour |
| Aug. 31 | S05 | 13:21-13:51 | 2 | 24 | 10-20 | W-NW | DET | 1 | 15 | 4 | moderate odour |
| Aug. 31 | S06 | 13:51-14:21 | 2 | 25 | 10-20 | W-NW | DET | 1 | 14 | 4 | strong odour |
| Aug. 31 | S07 | 14:22-14:52 | 2 | 25 | 10-20 | W-NW | 5 | 1 | 17 | 4 | strong odour |
| Aug. 31 | S08 | 14:54-15:24 | 2 | 25 | 10-20 | W-NW | DET | 1 | 17 | 4 | strong odour |
| Sep. 6 | S09 | 11:15-11:45 | 3 | 27 | 3-5 | S-SE | ND | 1 | 17 | 21 | slight odour |
| Sep. 6 | S10 | 11:45-12:15 | 3 | 27 | 3-5 | S-SW | ND | 1 | 4 | 21 | no odour |
| Sep. 6 | S11 | 12:16-12:46 | 3 | 27 | 3-6 | S-SW | ND | 1 | 19 | 21 | slight odour |
| Sep. 6 | S12 | 12:55-13:25 | 3 | 27 | 5-10 | S-SW | ND | 1 | 17 | 21 | slight odour |
| Sep. 6 | S13 | 13:25-13:55 | 3 | 27 | 5-10 | S-SW | ND | 1 | 13 | 21 | slight odour |
| Sep. 6 | S14 | 13:56-14:26 | 3 | 28 | 5-10 | S-SW | ND | 1 | 17 | 21 | slight odour |
| Sep. 6 | S15 | 14:37-15:07 | 3 | 28 | 6-12 | S-SW | ND | 1 | 12 | 21 | slight odour |
| Sep. 6 | S16 | 15:38-16:08 | 3 | 28 | 7-15 | S-SW | ND | 1 | 11 | 21 | slight odour |
| Sep. 7 | S17 | 10:15-10:45 | 1 | 25 | 5-10 | W-SW | ND | 0.7 | 9 | 13 | slight odour |
| Sep. 7 | S18 | 10:45-11:15 | 1 | 26 | 5-10 | W-SW | ND | 0.7 | 10 | 13 | slight odour |
| Sep. 7 | S19 | 11:17-11:47 | 1 | 26 | 5-10 | W-SW | ND | 0.7 | 1 | 13 | slight odour |
| Sep. 7 | S20 | 11:47-12:17 | 1 | 27 | 5-10 | W-SW | ND | 0.7 | 17 | 13 | slight odour |
| Sep. 7 | S21 | 12:18-12:48 | 1 | 27 | 5-10 | W-SW | ND | 0.7 | 7 | 13 | slight odour |
| Sep. 7 | S22 | 12:59-13:29 | 4 | 28 | 5-15 | W-SW | ND | 0.7 | 17 | 13 | slight odour |
| Sep. 7 | S23 | 13:29-13:59 | 4 | 28 | 5-15 | W-SW | ND | 0.7 | 15 | 13 | slight odour |
| Sep. 7 | S24 | 14:00-14:30 | 4 | 28 | 5-10 | W-SW | ND | 0.7 | 15 | 13 | slight odour |
| Sep. 7 | S25 | 14:30-15:00 | 4 | 29 | 0-10 | W-SW | ND | 0.7 | 10 | 13 | moderate odour |
| Sep. 7 | S26 | 15:00-15:30 | 4 | 30 | 5-10 | W-SW | ND | 0.7 | 6 | 13 | slight odour |
| Sep. 7 | S27 | 15:31-16:01 | 4 | 28 | 5-10 | W-SW | ND | 0.7 | 2 | 13 | slight odour |

1. See Figure 2 for downwind monitoring locations.

2. Meteorological conditions at 10 metres. AT = ambient temperature (°C).

WS = wind speed (km/hr) and WD = wind direction.

3. Units of µg/m³.

4. Units of µg/m³, based on 3σ (σ = standard deviation of background signal).

5. Maximum instantaneous concentration of 2-benzothiazole (units of µg/m³).

6. Uncertainty in 2-benzothiazole concentration, based on relative standard deviation of replicate calibration runs.

7. DET = above the detection limit, but below the quantitation limit (10σ).

8. NA = no data available.

9. No calibrations performed; data based on estimated response factors.

10. ND = not detected; below the detection limit (3σ).

Table 3: Half-hour Average Concentrations of Methylbenzothiazole.

| Date (1989) | Sample Number | Monitoring Period | Location ¹ | Metecological AT | WS | Conditions ² WD | 2-MBZl ³ ½hr Conc. | Det. ⁴ Limit | Max. ⁵ Conc. | Error ⁶ (RSD%) | Comments |
|-------------|---------------|-------------------|-----------------------|------------------|-------|----------------------------|-------------------------------|-------------------------|-------------------------|---------------------------|-----------------------------|
| Aug. 30 | S01 | 12:41-13:11 | 1 | 26 | 20-40 | W-NW | ND ¹⁰ | NA ⁸ | 5 | NA | moderate odour ⁹ |
| Aug. 30 | S02 | 13:12-13:42 | 1 | 25 | 20-30 | W-NW | ND | NA | 5 | NA | moderate odour ⁹ |
| Aug. 31 | S03 | 09:27-09:57 | 1 | 20 | 10-20 | W-NW | ND | 0.4 | 4 | 4 | moderate odour |
| Aug. 31 | S04 | 12:50-13:20 | 2 | 24 | 10-25 | W-NW | ND | 0.4 | 4 | 4 | moderate odour |
| Aug. 31 | S05 | 13:21-13:51 | 2 | 24 | 10-20 | W-NW | ND | 0.4 | 4 | 4 | moderate odour |
| Aug. 31 | S06 | 13:51-14:21 | 2 | 25 | 10-20 | W-NW | ND | 0.4 | 4 | 4 | strong odour |
| Aug. 31 | S07 | 14:22-14:52 | 2 | 25 | 10-20 | W-NW | ND | 0.4 | 5 | 4 | strong odour |
| Aug. 31 | S08 | 14:54-15:24 | 2 | 25 | 10-20 | W-NW | ND | 0.4 | 5 | 4 | strong odour |
| Sep. 6 | S09 | 11:15-11:45 | 3 | 27 | 3-5 | S-SE | ND | 0.3 | 4 | 14 | slight odour |
| Sep. 6 | S10 | 11:45-12:15 | 3 | 27 | 3-5 | S-SW | ND | 0.3 | 1 | 14 | no odour |
| Sep. 6 | S11 | 12:16-12:46 | 3 | 27 | 3-6 | S-SW | ND | 0.3 | 5 | 14 | slight odour |
| Sep. 6 | S12 | 12:55-13:25 | 3 | 27 | 5-10 | S-SW | ND | 0.3 | 5 | 14 | slight odour |
| Sep. 6 | S13 | 13:25-13:55 | 3 | 27 | 5-10 | S-SW | ND | 0.3 | 3 | 14 | slight odour |
| Sep. 6 | S14 | 13:56-14:26 | 3 | 28 | 5-10 | S-SW | ND | 0.3 | 6 | 14 | slight odour |
| Sep. 6 | S15 | 14:37-15:07 | 3 | 28 | 6-12 | S-SW | ND | 0.3 | 4 | 14 | slight odour |
| Sep. 6 | S16 | 15:38-16:08 | 3 | 28 | 7-15 | S-SW | ND | 0.3 | 4 | 14 | slight odour |
| Sep. 7 | S17 | 10:15-10:45 | 1 | 25 | 5-10 | W-SW | ND | 0.06 | 2 | 4 | slight odour |
| Sep. 7 | S18 | 10:45-11:15 | 1 | 26 | 5-10 | W-SW | ND | 0.06 | 3 | 4 | slight odour |
| Sep. 7 | S19 | 11:17-11:47 | 1 | 26 | 5-10 | W-SW | ND | 0.06 | ND | 4 | slight odour |
| Sep. 7 | S20 | 11:47-12:17 | 1 | 27 | 5-10 | W-SW | DET ⁷ | 0.06 | 3 | 4 | slight odour |
| Sep. 7 | S21 | 12:18-12:48 | 1 | 27 | 5-10 | W-SW | ND | 0.06 | 1 | 4 | slight odour |
| Sep. 7 | S22 | 12:59-13:29 | 4 | 28 | 5-15 | W-SW | DET | 0.06 | 3 | 4 | slight odour |
| Sep. 7 | S23 | 13:29-13:59 | 4 | 28 | 5-15 | W-SW | DET | 0.06 | 3 | 4 | slight odour |
| Sep. 7 | S24 | 14:00-14:30 | 4 | 28 | 5-10 | W-SW | ND | 0.06 | 2 | 4 | slight odour |
| Sep. 7 | S25 | 14:30-15:00 | 4 | 29 | 0-10 | W-SW | DET | 0.06 | 3 | 4 | moderate odour |
| Sep. 7 | S26 | 15:00-15:30 | 4 | 30 | 5-10 | W-SW | ND | 0.06 | 2 | 4 | slight odour |
| Sep. 7 | S27 | 15:31-16:01 | 4 | 28 | 5-10 | W-SW | ND | 0.06 | DET | 4 | slight odour |

1. See Figure 2 for downwind monitoring locations.

2. Meteorological conditions at 10 metres: AT = ambient temperature (°C), WS = wind speed (km/hr) and WD = wind direction.

3. Units of $\mu\text{g}/\text{m}^3$.4. Units of $\mu\text{g}/\text{m}^3$, based on 3σ (σ = standard deviation of background signal).5. Maximum instantaneous concentration of 2-methylbenzothiazole (units of $\mu\text{g}/\text{m}^3$).

6. Uncertainty in 2-methylbenzothiazole concentration, based on the relative standard deviation of replicate calibration runs.

7. DET = above the detection limit, but below the quantitation limit (10 μg).

8. NA = no data available.

9. No calibrations performed; data based on estimated response factors.

10. ND = not detected, below the detection limit (3 σ).

Table 4: Half-hour Average Concentrations of Trimethylamine.

| Date (1989) | Sample Number | Monitoring Period | Location ¹ | Meteorological AT | Conditions ² WS WD | TMA ³ ½hr Conc. | Det. ⁴ Limit | Max. ⁵ Conc. | Error ⁶ (RSD%) | Comments ⁹ |
|----------------|------------------|----------------------|-----------------------|----------------------|----------------------------------|-------------------------------|----------------------------|----------------------------|------------------------------|-----------------------|
| Aug. 30 | S01 | 12:41-13:11 | 1 | 26 | 20-40 | W-NW | NA ⁸ | 1.64 | 2 | moderate odour |
| Aug. 30 | S02 | 13:12-13:42 | 1 | 25 | 20-30 | W-NW | NA | 1.54 | 2 | moderate odour |
| Aug. 31 | S03 | 09:27-09:57 | 1 | 20 | 10-20 | W-NW | 0.73 | 2.75 | 2 | moderate odour |
| Aug. 31 | S04 | 12:50-13:20 | 2 | 24 | 10-25 | W-NW | DET ⁷ | 1.01 | 2 | moderate odour |
| Aug. 31 | S05 | 13:21-13:51 | 2 | 24 | 10-20 | W-NW | DET | 1.21 | 2 | moderate odour |
| Aug. 31 | S06 | 13:51-14:21 | 2 | 25 | 10-20 | W-NW | 0.50 | 2.03 | 2 | strong odour |
| Aug. 31 | S07 | 14:22-14:52 | 2 | 25 | 10-20 | W-NW | 0.90 | 2.44 | 2 | strong odour |
| Aug. 31 | S08 | 14:54-15:24 | 2 | 25 | 10-20 | W-NW | 0.71 | 2.35 | 2 | strong odour |
| Sep. 6 | S09 | 11:15-11:45 | 3 | 27 | 3-5 | S-SE | 1.83 | 11.05 | 2 | slight odour |
| Sep. 6 | S10 | 11:45-12:15 | 3 | 27 | 3-5 | S-SW | 1.02 | 6.73 | 2 | no odour |
| Sep. 6 | S11 | 12:16-12:46 | 3 | 27 | 3-6 | S-SW | 1.13 | 7.12 | 2 | slight odour |
| Sep. 6 | S12 | 12:55-13:25 | 3 | 27 | 5-10 | S-SW | 0.84 | 3.64 | 2 | slight odour |
| Sep. 6 | S13 | 13:25-13:55 | 3 | 27 | 5-10 | S-SW | 0.60 | 4.10 | 2 | slight odour |
| Sep. 6 | S14 | 13:56-14:26 | 3 | 28 | 5-10 | S-SW | DET | 1.18 | 2 | slight odour |
| Sep. 6 | S15 | 14:37-15:07 | 3 | 28 | 6-12 | S-SW | DET | 2.06 | 2 | slight odour |
| Sep. 6 | S16 | 15:38-16:08 | 3 | 28 | 7-15 | S-SW | DET | 2.19 | 2 | slight odour |
| Sep. 7 | S17 | 10:15-10:45 | 1 | 25 | 5-10 | W-SW | ND ¹⁰ | 0.32 | 2 | slight odour |
| Sep. 7 | S18 | 10:45-11:15 | 1 | 26 | 5-10 | W-SW | ND | 0.73 | 2 | slight odour |
| Sep. 7 | S19 | 11:17-11:47 | 1 | 26 | 5-10 | W-SW | ND | ND | 2 | slight odour |
| Sep. 7 | S20 | 11:47-12:17 | 1 | 27 | 5-10 | W-SW | ND | 0.53 | 2 | slight odour |
| Sep. 7 | S21 | 12:18-12:48 | 1 | 27 | 5-10 | W-SW | ND | 1.53 | 2 | slight odour |
| Sep. 7 | S22 | 12:59-13:29 | 4 | 28 | 5-15 | W-SW | ND | 0.84 | 2 | slight odour |
| Sep. 7 | S23 | 13:29-13:59 | 4 | 28 | 5-15 | W-SW | ND | 0.49 | 2 | slight odour |
| Sep. 7 | S24 | 14:00-14:30 | 4 | 28 | 5-10 | W-SW | ND | 0.43 | 2 | slight odour |
| Sep. 7 | S25 | 14:30-15:00 | 4 | 29 | 0-10 | W-SW | ND | 0.73 | 2 | moderate odour |
| Sep. 7 | S26 | 15:00-15:30 | 4 | 30 | 5-10 | W-SW | ND | 0.32 | 2 | slight odour |
| Sep. 7 | S27 | 15:31-16:01 | 4 | 28 | 5-10 | W-SW | ND | 0.22 | 2 | slight odour |

1. See Figure 2 for downwind monitoring locations.

2. Meteorological conditions at 10 metres. AT = ambient temperature (°C).

3. WS = wind speed (km/h) and WD = wind direction.

4. Units of $\mu\text{g}/\text{m}^3$.5. Maximum instantaneous concentration of trimethylamine (units of $\mu\text{g}/\text{m}^3$).

6. Uncertainty in trimethylamine concentration, based on relative standard deviation of replicate calibration runs.

7. DET = above the detection limit, but below the quantitation limit (10 μ).

8. NA = no data available.

9. No calibrations performed; data based on estimated response factors.

10. ND = not detected, below the detection limit (3 σ).

Figure 1: Schematic of the TAGA 6000 System.

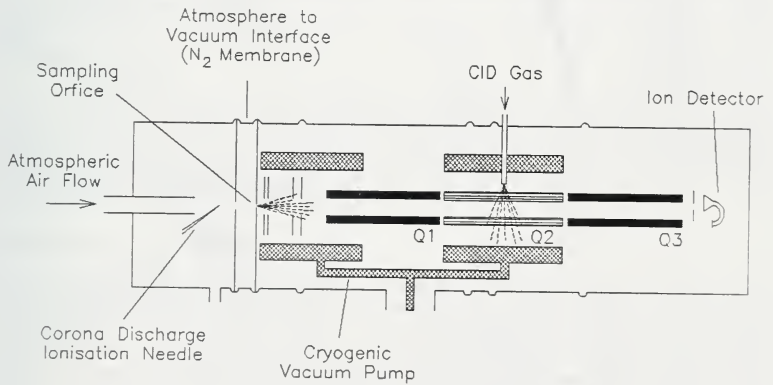
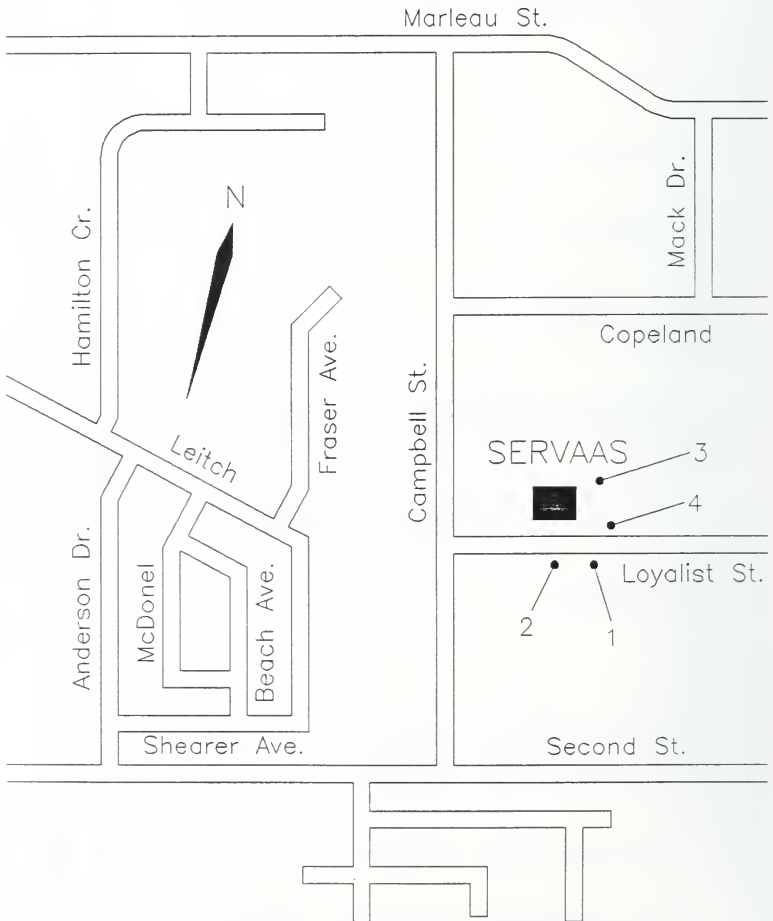


Figure 2: Map of the Monitoring Sites at SerVaas Rubber Canada Plant.



6.0 Appendices

6.1 Appendix A: Plant Process and Relevant Production Information.

Plant Process

SerVaas Rubber Canada, Inc. manufactures butyl reclaim from scrap butyl inner tubes. The reclaim process thermally degrades the cured butyl rubber into a soft plastic state. Some of the crosslinked bonds and butyl polymer bonds are broken through a chain scission mechanism. The reclaim retains the same chemical properties and approximately 75% of the physical properties of the original compound.

The manufacturing process consists of the following steps: chopping, autoclaving, batching/milling, and finishing.

Chopping

Devalved scrap butyl inner tubes are shredded by a high speed chopper into 1cm pellet-like particles. Pneumatic air cools the mechanical parts of the chopper and transports the rubber from the chopper to a cyclone. The cyclone unit separates the rubber particles from the air. Some dust particles mixed with the air are vented to the atmosphere. The rubber is transferred by auger and stored in bins.

Autoclave

Approximately 3000kg of shredded rubber from the storage bins are mixed with 0 to 70kg of Sunthene 450 naphthalenic oil and 35kg of CaCO_3 . The exact oil amount is dependent on the type of scrap tubes. The rubber mixture is placed in a vessel (boat) which fits into the autoclave. Saturated steam is the heating agent inside the autoclave for the thermal degradation reactions (devulcanisation). Approximately 400L of condensed liquid collected from previous devulcanisation cycles is pumped into the autoclave. The reaction conditions are 190°C to 200°C (13 to 15 atmospheres) for 3.5 to 5 hours. At the end of the cycle the pressure is slowly released by venting the steam from the autoclave through a condenser (blowdown). The liquid condensate is stored for reuse in subsequent autoclave cycles.

Batching/Milling

After the autoclave cycle the rubber from the boat is emptied into the cake breaker. This breaks up any rubber agglomerations into rubber particles. The rubber particles are batched through a strainer which is an extruder with a screen at the outlet. An 8 mesh screen removes all large foreign matter from the rubber. After straining the rubber is milled. A mill is a parallel set of rollers turning in opposite directions. One of

the rollers turns at a slightly increased speed over the other roller to create friction. The plant is equipped with 2 breakdown mills that feed 8 refining mills. The breakdown mills sheet the rubber at 0.5mm while the refining mills sheet the rubber at 0.1mm.

Finishing

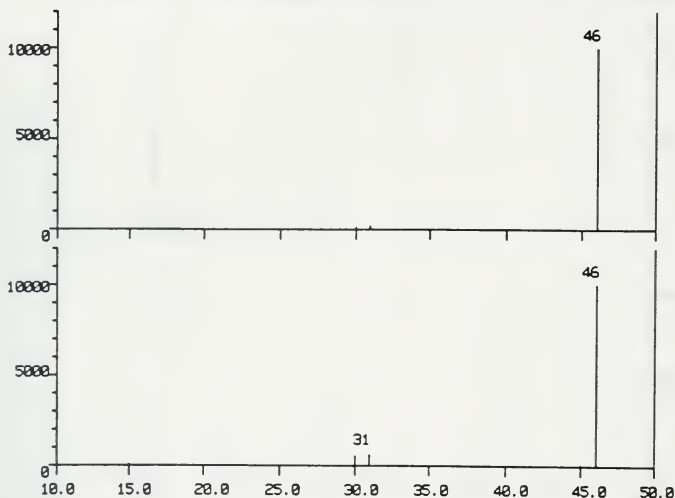
The processed rubber from the 8 refiner mills passes through a second strainer containing a 1mm plate. This step removes all remaining foreign material from the reclaim. A final extruder shapes the reclaim into slabs for packaging.

Relevant Production Information

It was confirmed by the Southeastern Region that the SerVaas Rubber Plant was in full operation during the period of August 29, 1989 to September 8, 1989 except for the weekend period of September 2 and 3. The plant was shut down during September 2 and 3 (Saturday and Sunday). On all other days the plant was operating on a 24 hour basis.

6.2 Appendix B: TAGA 6000 Library Search Daughter Ion Scans of the Odour Fingerprint Compounds, SerVaas Rubber, Cornwall.

C063104.DA

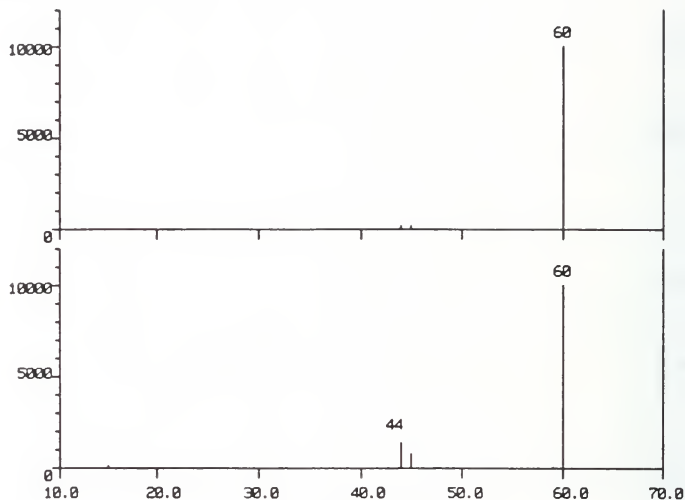


Library Search Results

Library File: SCILIB2 Parent Ion : 46

| Name | Formula | Index | M.W. | Reverse | Forward |
|----------------|----------|-------|------|---------|---------|
| DIMETHYL AMINE | C2.H7.N | 229 | 45 | 0.8944 | 0.8281 |
| ETHYL AMINE | C2.H7.N | 234 | 45 | 0.1925 | 0.3381 |
| FORMAMIDE | C.H3.O.N | 35 | 45 | 0.1644 | 0.0000 |

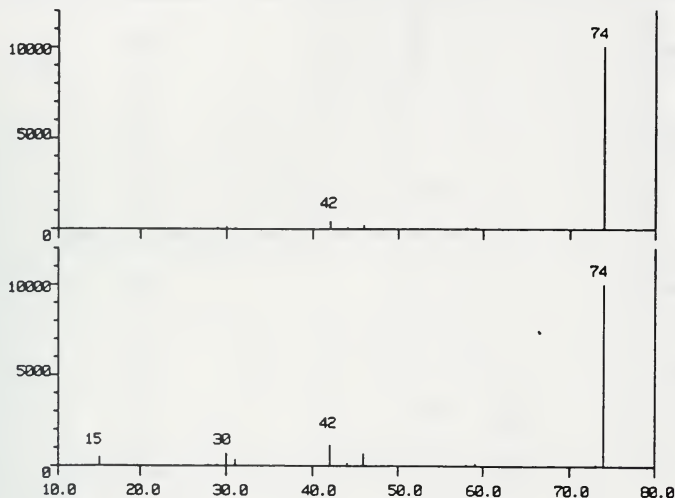
COR3000.DA



Library Search Results

Library File: SCILIB2 Parent Ion : 60

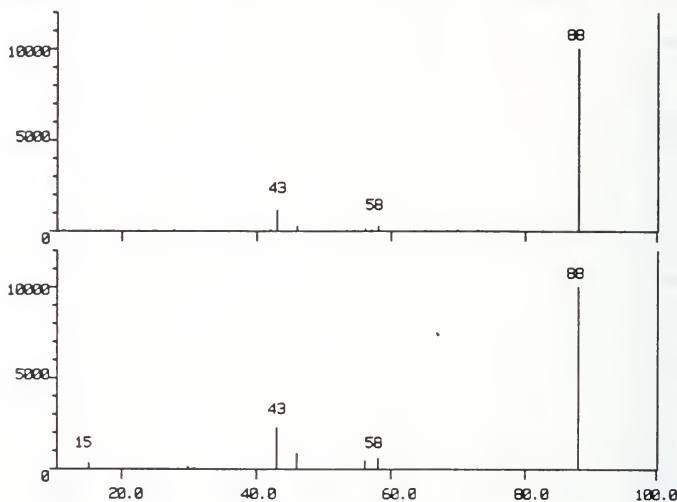
| <u>Name</u> | <u>Formula</u> | <u>Index</u> | <u>M.W.</u> | <u>Reverse</u> | <u>Forward</u> |
|-----------------|----------------|--------------|-------------|----------------|----------------|
| TRIMETHYL AMINE | C3.H9.N | 221 | 59 | 0.7687 | 0.9661 |

Library Search Results

Library File: SCILIB2 Parent Ion : 74

| <u>Name</u> | <u>Formula</u> | <u>Index</u> | <u>M.W.</u> | <u>Reverse</u> | <u>Forward</u> |
|-----------------------|----------------|--------------|-------------|----------------|----------------|
| N,N-DIMETHYLFORMAMIDE | C3.H7.O.N | 30 | 73 | 0.8723 | 0.7591 |
| DIETHYL AMINE | C4.H11.N | 109 | 73 | 0.6633 | 0.3906 |
| s-BUTYL AMINE | C4.H11.N | 120 | 73 | 0.5316 | 0.2911 |
| t-BUTYL AMINE | C4.H11.N | 117 | 73 | 0.5058 | 0.1841 |
| n-BUTYL AMINE | C4.H11.N | 125 | 73 | 0.4867 | 0.3682 |
| ISOBUTYL AMINE | C4.H11.N | 123 | 73 | 0.4714 | 0.1841 |

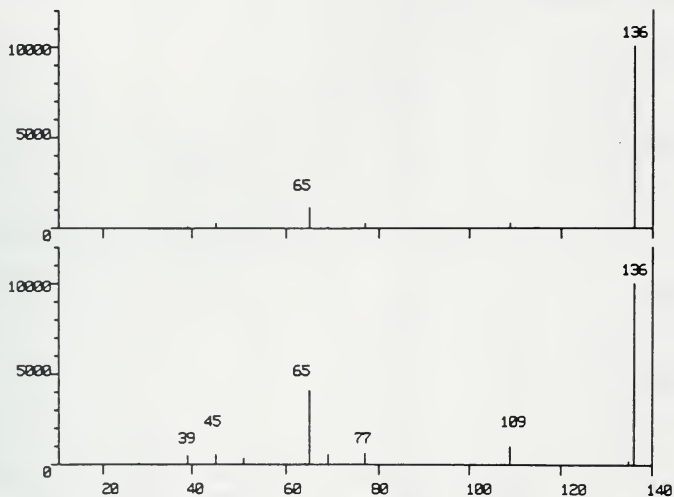
COR3107.DA



Library Search Results

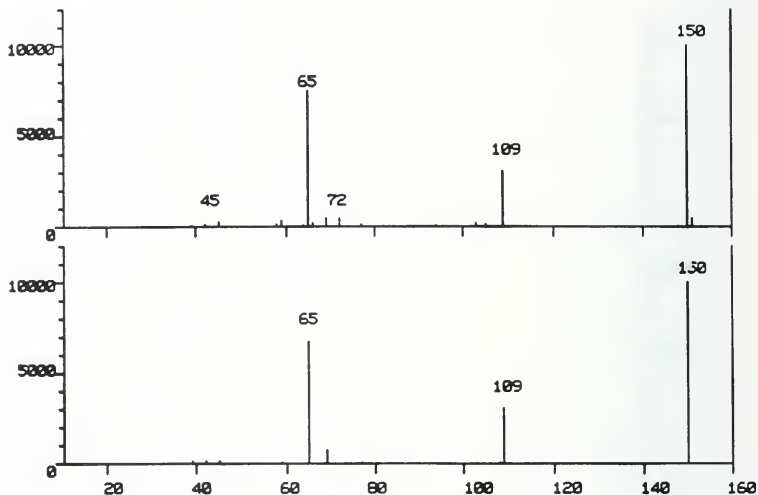
Library File: SCILIB2 Parent Ion : 88

| Name | Formula | Index | M.W. | Reverse | Forward |
|--------------------|-----------|-------|------|---------|---------|
| DIMETHYL ACETAMIDE | C4.H9.O.N | 140 | 87 | 0.7829 | 0.7829 |
| ISOPENTYL AMINE | C5.H13.N | 112 | 87 | 0.5145 | 0.6222 |
| PENTYL AMINE | C5.H13.N | 116 | 87 | 0.4939 | 0.5957 |
| MORPHOLINE | C4.H9.N.O | 182 | 87 | 0.2236 | 0.3532 |

Library Search Results

Library File: SCILIB2 Parent Ion : 136

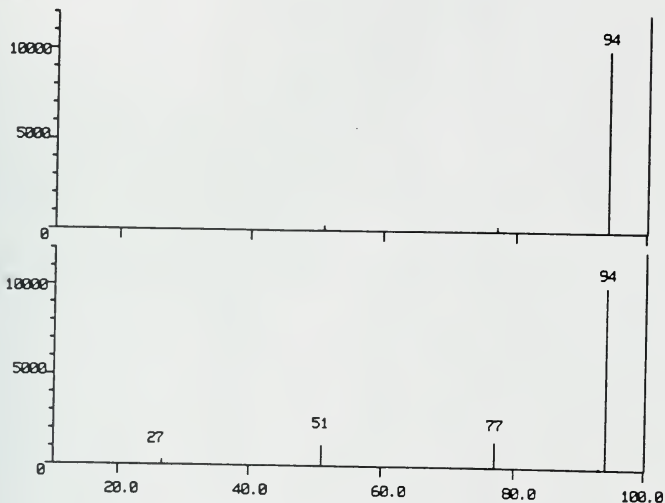
| <u>Name</u> | <u>Formula</u> | <u>Index</u> | <u>M.W.</u> | <u>Reverse</u> | <u>Forward</u> |
|----------------|----------------|--------------|-------------|----------------|----------------|
| 2-BENZOTHAZOLE | C7,H5,N,S | 211 | 135 | 0.8563 | 0.8510 |

Library Search Results

Library File: SCILIB2 Parent Ion : 150

| <u>Name</u> | <u>Formula</u> | <u>Index</u> | <u>M.W.</u> | <u>Reverse</u> | <u>Forward</u> |
|-----------------------|----------------|--------------|-------------|----------------|----------------|
| 2-METHYL BENZOTHAZOLE | C8.H7.N.S | 384 | 149 | 0.9535 | 0.8238 |

C053016.DA



Library Search Results

Library File: SCILIB2 Parent Ion : 94

| Name | Formula | Index | M.W. | Reverse | Forward |
|---------|---------|-------|------|---------|---------|
| ANILINE | C6.H7.N | 214 | 93 | 0.7483 | 0.9682 |

